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Cool water-splitting by microwaves

Microwave heating has become a useful tool in catalysis to obtain chemical products under unconventional reaction conditions. Now, researchers have demonstrated low-temperature water-splitting to produce hydrogen using microwave catalysis and revealed the important role of reduced oxides in the process.

Daniel R. Slocombe

The majority of hydrogen produced globally is made by the reforming of methane, which releases almost the same amount of CO₂ as it does hydrogen in the process. Producing hydrogen from water using green energy is seen as a sustainable alternative, but has some drawbacks. For example, water-splitting by electrolysis is a well-established and low-carbon route to hydrogen production [1], but is highly energy intensive; thermochemical routes require very high temperatures [2]. Now, writing in *Nature Energy*, Jose M. Serra, José M. Catalá-Civera and colleagues at Universitat Politècnica de València report a microwave method that uses oxide catalysts to liberate hydrogen from water at remarkably low temperatures [3].

Microwave heating initiates very different mechanisms from conventional thermal approaches and can lead to dramatically different results at seemingly lower temperatures. In the heating of heterogeneous mixtures this is often attributed to highly localised heating at regions of high polarisation around features and interfaces and can have advantageous results in some catalytic reactions. This effect has been observed in many chemical processes, including, for example, the production of hydrogen by the dehydrogenation of waxes and other hydrocarbons [4-6].

Serra, Catalá-Civera and colleagues set out an exciting method of releasing hydrogen from water by microwave redox activation of solid-state ionic materials based on Gd-doped ceria (CGO). The process operates in two steps: first, microwave treatment partially reduces the CGO and creates oxygen vacancies, which leads to an increase in charge carriers and associated electrical conductivity; second, the activated material is re-oxidised as it spontaneously reacts with water at elevated temperature to form H₂.

The researchers report that the process occurs at a temperature below 250 °C. However, it is likely that the local temperature at reaction sites is somewhat higher than this, since the temperature in microwave fields can only be measured by infrared pyrometry or fibre optics,

which have a finite footprint over which the measurement will be averaged. Indeed, this is the basis of one of the major advantages of microwave heating: process intensification by highly local heating, whilst maintaining a lower bulk sample temperature.

Interestingly, the researchers observe an apparently intimate link between the reduction of the oxide, an increase in conductivity, and the mechanism of hydrogen release. Online measurements indicate a rapidly increasing catalyst conductivity at elevated temperatures, induced by the microwave heating, and reveal the important role of the redox cycle and associated charge carriers in the liberation of hydrogen from water. These measurements demonstrate a key concept in microwave catalysis of an induction temperature ($\sim 110\text{ }^{\circ}\text{C}$ in this case) at which the rate of energy absorption increases and leads to thermal runaway. In turn, this provides the higher temperatures required for reduction and subsequent oxidation of the CGO.

Self-doping by oxygen vacancies caused by treatment in a reducing atmosphere is a common feature of many conducting oxides and typically leads to increased conductivity. The associated imaginary permittivity – which is directly connected to the heating rate of the material in microwaves – will increase with increasing conductivity for moderately conducting materials, like CGO. Thus, the researchers find that prior microwave reduction of the CGO catalyst leads to an increased heating rate and activation of the material in microwaves. As they discuss, the principle is quite general and can be applied in many reactions to directly produce different molecular energy carriers, e.g. in converting H_2O and CO_2 into syngas, which can in turn be transformed into hydrocarbons.

The researchers carried out thermodynamic process simulations to evaluate energy efficiency and assess the practical implications of the microwave assisted water-splitting. The simulations reveal that the difference in enthalpies between oxygen-vacancy generation and water dissociation is exothermic ($\Delta H_r > \Delta H_{\text{H}_2\text{O}}$), with surplus heat energy recovered in the next endothermic reduction cycle. Dopant type and strength were also shown to affect the reduction enthalpy of the oxide lattice, greatly influencing the energy requirements of the reaction. Figure 1 shows the simplified energy flow in the process, where the green branch is the fraction of absorbed microwave energy used directly in the reduction of the oxide. The microwave energy fraction not used in the reduction of the catalyst is reused to supply the heat energy demand of the water splitting reaction.

Microwave enhanced processes such as this often raise questions about the energy cost, or the efficiency of the technique. Serra, Catalá-Civera and team provide a compelling

discussion in which the operating energy costs are compared with established technologies for H₂ production from water: electrolysis plants based on alkaline and proton exchange membrane cells and a solar thermochemical plant based on ceria and perovskite oxides. The quantitative analysis of the operating energy costs of this new microwave technology show that it could be competitive with conventional water electrolysis techniques in the future.

However, the microwave energy must be selectively used to reduce the oxide rather than being absorbed by other heating processes. In this way, operating energy costs are optimised and a higher efficiency can be reached than, for example, experimental solar thermal processes. Achieving this represents an important scientific challenge, which must be confronted before the application of this technology is fully realised. Strategies to use the microwave energy even more selectively and therefore more efficiently remain elusive and require a deeper understanding of the microwave reduction process only obtainable by further studies. Nonetheless, this work sets out a strong foundation from which to develop understanding and control of these reactions, and it will be fascinating to see how microwave driven catalytic processes in hydrogen production and other emerging applications improve over the coming years.

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Competing interests

The author declares no competing interests

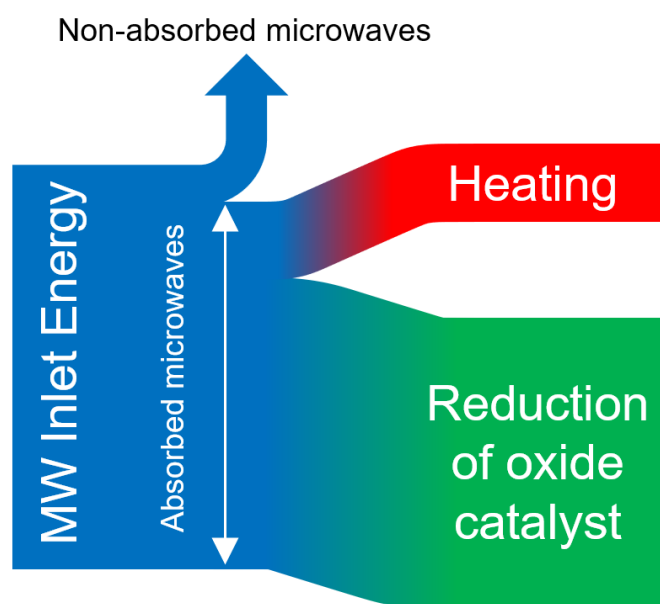


Figure 1. Simplified energy flow diagram for microwave-assisted reduction of an oxide catalyst for hydrogen production. The key to optimising the efficiency of the process is to ensure that microwave energy is selectively used to reduce the oxide rather than being absorbed by other heating processes [Adapted from reference 3 with permission].

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